16 in. onto the sample. The rebound percent was read on the height scale.

Percent Open Cells. The method and apparatus of Remington and Pariser (11) were employed, and duplicate determinations were performed following ASTM D 1940-62T, except that the sample for each determination consisted of two 7-cm^3 specimens.

Discussion

Physical properties and test results on the foams are listed in Table II. Dimensional stability after humid aging was greatest for foams from the dioxyethylene polyols. Stability increased, however, with prepolymer viscosity, since dimensional change was least at each degree of polyol oxyethylation for the 53,000 cps-viscosity prepolymer.

Trends of density, compressive strength, energy rebound, and water absorption are compared graphically in Figure 1, as functions of polyol oxyethylation, n, for the three prepolymer viscosities. Average densities ranged from 1.64 to 2.08 lb/ft^3. The curves were convex, being higher at 4 and 6, and lower at 2 and 8 oxyethylene units. Densities also paralleled the viscosities of the prepolymers used.

Average compressive strengths at 25% compression ranged from 29 to 65 lb/in^2, with a maximum in each prepolymer series at 4.25 polyol oxyethylene units. In general highest values were obtained from the 32,000 cps prepolymer. Compressive strengths appear to be in a satisfactory range for rigid foams. Since the densities of most of these foams were below 2 lb/ft^3, the use of somewhat less Freon would presumably lead to foams of still acceptable density and even higher compressive strengths.

Energy rebound varied with *n* in the same fashion as density. For each viscosity, water absorption decreased linearly to a striking minimum at 6 oxyethylene units. The inverse of these curves, measuring resistance to water absorption would be more comparable to the curves for the positive properties. Increase in prepolymer viscosity caused less water to be absorbed.

The results reported show that rigid foams of satisfactory low density and good compressive strength can be made from oxyethylated *threo*-9,10-dihydroxystearic acid, triisopropanolamine, and prepolymers based on oxypropylated sorbital and tolylene diisocyanate. A moderate range of properties was obtained by varying degree of polyol oxyethylation and prepolymer viscosity.

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REFERENCES

1. Swern, D., G. N. Billen, T. W. Findley and J. T. Scanlan, J. Am. Chem. Soc. *67*, 1786–1789 (1945).
2. Traynard, J. C., Bull. Soc. Chim. France 323–324 (1952).
3. Wrigley, A. N., F. D. Smith and A. J. Stirton, JAOCS *39*, 80–84 (1962).
4. Shechter, L., and J. Wynstra, Ind. Eng. Chem. *48*, 86–93 (1956).
5. Wrigley, A. N., F. D. Smith and A. J. Stirton, JAOCS *34*, 39–43 (1957).
6. Malkemus, J. D., and J. D. Swan, *Ibid. 34*, 342–344 (1957).
7. Wrigley, A. N., F. D. Smith and A. J. Stirton, *Ibid. 36*, 34–36 (1959).
8. Yeadon. D. A., W. F. McSherry and L. A. Goldblatt, *Ibid. 36*, 16–20 (1959).
9. Lyon, C. K., V. H. Garrett and L. A. Goldblatt, *Ibid. 41*, 23–25 (1964).
10. Saunders, J. H., and K. C. Frisch, "Polyurethanes: Chemistry and Technology, Part I" ("High Polymers," Vol. 16), Interscience Publishers, New York, 1962, 63–128.
11. Remington, W. J., and R. Pariser, Rubber World *138*, 261–264 (1958).

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Hydrogenation of Cottonseed Oil With Reused Catalyst

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Abstract

Cottonseed oil was hydrogenated using both new (Rufert catalyst flakes) and reused (up to five uses) catalysts at 130–169C, at a pressure of 45 psig, and with high degrees of agitation.

The activity of the catalyst increased initially with use, especially at 130C, but with continued use the activity decreased. The selectivity of the hydrogenation decreased with reuse of the catalyst, especially at lower temp. Isomerization decreased slightly as the catalyst was used only at higher temps. The induction period found with fresh catalyst at 130C was eliminated in runs with second- and third-use catalyst. A small induction period was noted with fifth-use catalyst.

Treatment of once-use catalyst with air severely reduced the catalyst activity. Steam- and vacuum-treatment of the catalyst resulted in a slightly less active catalyst than a hydrogen-treated catalyst. None of these treatments significantly affected selectivity or isomerization.

Results of this investigation can be explained in large part by the concn of hydrogen absorbed on the catalyst surface.

Introduction

Nickel catalysts for the hydrogenation of triglycerides are commonly used industrially at least several times. With oils that have been carefully refined and bleached to remove catalyst poisons, the catalyst is often used 10, 20 or even more times. Hence, 90% or more of the hydrogenations are made with used catalyst. Yet the literature pertaining to used catalysts is meagre.

Factors which are of importance when the catalyst is reused include the amt and type of poison in the oil or hydrogen. Poisons which are sometimes present in the oil include free fatty acids, cartenoid-type compounds, alkali salts and sulfur compounds (4). Modern refining and bleaching techniques are generally effective in removing most, but not necessarily all, of the poisons from the raw oils. Besides catalyst poisons, used catalysts probably lose their activity because of just repeated uses, i.e., they just get "tired" with continued use. The activity of the used catalyst (ability of the catalyst to add hydrogen to the oil at a rapid rate) and the type of hydrogenation obtained (degree of selectivity and of isomerization) probably vary to a considerable extent with the past history of the catalyst.

Bailey (4) defines selectivity as applied to cata-

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lysts in a manner which is inconsistent with his definition of selective hydrogenation and with the definition of selective hydrogenation that is normally accepted. He presents hydrogenation data obtained with several used catalysts, but the history of these catalysts and the method of hydrogenation employed are not clear. His discussion on how selectivity of hydrogenation is affected by used catalysts is hence open to question.

A general rule of the hydrogenation industry is that the hydrogenations become less selective as the catalyst is reused. Yet no literature is known that describes investigations which have unequivocally studied the several factors related to reused catalysts in regards to selectivity and isomerization. For example, two explanations are possible why selectivity decreases with catalyst use:

1) The surfaces of the catalyst change with use so that the reactions occurring there will produce less selective hydrogenation.
2) Decreased selectivity is related to the loss of activity. As has been pointed out repeatedly (2,3,6,9), mass transfer is a highly important factor in hydrogenations with relatively low degrees of agitation. Loss of catalyst activity allows greater concn of the hydrogen in the oil and at the catalyst surface. Bailey (4) in 1950 and Eckey (5) in 1954 postulated that higher concn of hydrogen at the catalyst surface would cause decreased selectivity. Albright and coworkers (3,6,9) later conclusively proved that this was actually true. Isomerization is also related to the concn of hydrogen at the catalyst surface.

Since hydrogenations with used catalysts are still rather poorly understood theoretically, the present investigation was made to study the effect of reusing nickel catalysts on the rate of hydrogenation, selectivity and degree of isomerization. A reactor was employed which provided high degrees of agitation so that the above two explanations could be evaluated when the catalyst was recovered and reused. Subjecting the catalysts to hydrogen, steam, air and a vacuum between runs was also investigated.

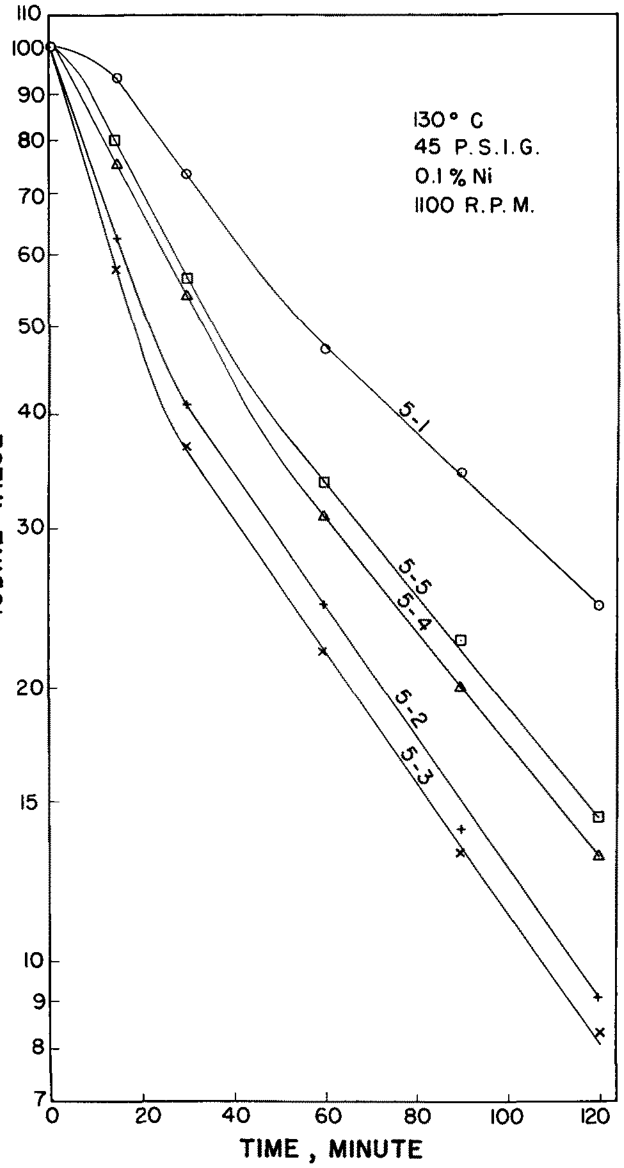

FIG. 1. Effect of reused catalyst on reaction rate at 130C.

Equipment and Operating Procedure

The dead-end hydrogenator and auxiliary equipment used were essentially identical to that used earlier by Albright et al. (2). The refined and bleached cottonseed oil used in this research was obtained from The Procter & Gamble Co. Three oils were used which are as follows: Oil A with an I.V. (iodine value—Wijs) of 102.1; Oil B with an I.V. of 105.7; and Oil C with an I.V. of 108.7. The hydrogen used was electrolytic grade and was purchased from the Matheson Co. The purity of this hydrogen was reported to be 99.8%. The catalyst flakes used were prepared by Harshaw Chemical Co.; 25.3% nickel was dispersed in the hardened oil flakes. Celite analytical filter aid (manufactured by John-Mansville Corp.) was used for recovery of the catalyst from the hydrogenated oil.

The operating procedures for the hydrogenation were similar to those used earlier (2). Slight modification had to be made to secure complete recovery of the catalyst from each hydrogenated oil sample. A total of 4 to 7 hydrogenated samples were taken for each run and all samples were filtered through the same filter paper. Approx 15 sec before a sample was to be taken, 5 ml of hydrogenated oil was removed through the sampling valve at the bottom of the reactor. This sample was filtered, and the oil was discarded. It was assumed that this 5 ml of oil would act to flush out most of the oil from the previous sample. Another 5 ml sample was then taken. This oil sample was filtered, and the filtrate was collected and was considered to be the sample at the desired time.

The hydrogenated oil samples were analyzed for I.V. by the standard Wijs method. Gas chromatographic and IR analyses were made by Swift & Co. of the fatty acid composition and of the total *trans*-isomers respectively of various oil samples.

Results

A total of 16 series of runs were made at the following conditions:

Temp: 130–169C
Pressure: 45 psig of hydrogen
Catalysts: nickel concn 0.1% (by wt based on the oil charged)
Agitation: 1100 rpm

The runs were numbered as Run X-Y, where X is the series number and Y is the number of times the

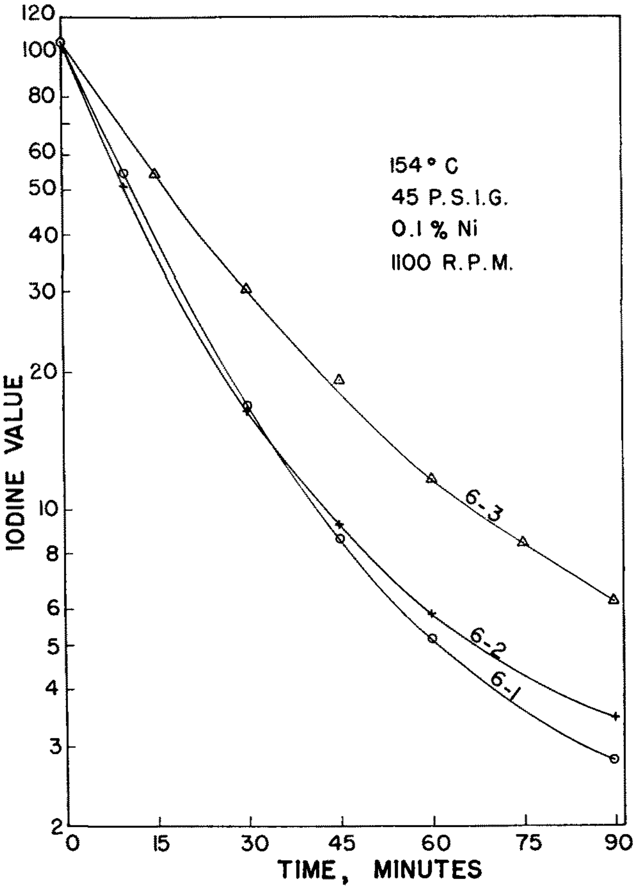

FIG. 2. Effect of reused catalyst on reaction rate at 154C.

catalyst was used at the end of the run. Preliminary runs (Series 1 through 4) were made with Oil A. Oil B was used for Series 5 through 8, and Oil C was used for the remaining runs.

Hydrogenation results with fresh (or first-use) catalyst were similar to those of Albright et al. (2) who also used comparable rates of agitation. An induction period of 8 min occurred at 130C (See Run 5-1 of Fig. 1) and of 0.3 min at 154C (Run 6-1 of Fig 2). No detectable induction period was noted at 169C, as is indicated by Run 7-1 of Figure 3. Later repeat runs at these temp gave essentially identical results.

Reused Catalysts. At 130C, no induction period occurred for second- and third-use catalyst; Figure 1 indicates the results for Runs 5-2 and 5-3. Two other later series of runs also gave the same results. An induction period of ca. one min was obtained in Run 5-4; the induction period increased to ca. 4.5 min in Run 5-5. The rates of hydrogenation for Runs 5-2, and especially 5-3, were considerably faster than those for Run 5-1 with new catalyst; even Runs 5-4 and 5-5 with fourth- and fifth-use catalyst, respectively, had faster rates of hydrogenation than Run 5-1. After the third use, the activity of the catalyst decreased with further use.

The shapes of curves for runs at 154C (see Fig. 2) and at 169C (see Fig. 3) were essentially the same with used catalyst as with the new catalyst. The only difference was that during the initial portion of the curve the rate of hydrogenation was slightly greater with the used catalyst than with fresh catalyst. During the later portion of the run, however, the rate of hydrogenation for the used catalyst was somewhat slower than that with the new catalyst.

Rate Constants. Assuming first order reaction rate kinetics, instantaneous rate constants were calculated as follows:

$$r = \frac{-d(\text{I.V.})}{dt} = k' \, (\text{I.V.})$$

where k′ is the negative of the slope of plots such as in Figures 1, 2 and 3. Plots of k′, the instantaneous rate constant vs. time, were useful in evaluating the activity of the catalyst as a function of the time of hydrogenation. Runs 5-1, 5-4 and 5-5 had low values of k′ during the initial stages of the runs because of the induction period. The values, however, increased after the initial stage to a maximum before decreasing to a constant value. Run 5-2 started with a higher value of k′ which remained almost constant to ca. 50 I.V. and then fell to another constant value of k′ at ca. 35 I.V. The values of k′ for Run 5-3 were higher during the initial portion of the run than those for Run 5-2; but the two runs had ca. the same reaction rate constant below 35 I.V. The same pattern was obtained for other runs at 130C even though the oils were different and the catalysts were also treated in one case (Run 13-2) with steam, as will be discussed later.

Values of k′ for Runs 6-1, 6-2 and 6-3 at 154C with Oil B were constant in each of the three runs to approximately 55 I.V. The values then dropped as the I.V. became lower. The catalyst activity of Run 6-2 was higher down to ca. 30 I.V. than that for Run 6-1. The activity of the catalyst in Run 6-3 was constantly below the activity of the catalyst in Run 6-1. At temps of 166-169C, difficulty was encountered in accurately determining the initial slopes of the curves such as in Figure 3 because the reaction was so rapid. At the beginning of these runs with once-used catalysts, k′ values were higher than those obtained with fresh catalysts. The values dropped slowly, however, as the I.V. became lower. Runs 7-1 and 7-2 had the same value of k′ at ca. 60 I.V.

Time Between Runs in a Series. In Series 5 and in Series 8 (each made at 130C), the time between the runs seemed to affect the activity of the resused catalysts. For example, Run 5-4 was performed ca. a day after Run 5-3, and the rate of reaction was significantly lower for Run 5-4. Run 5-5 followed Run 5-4 by only two hr, and Figure 1 indicates these two runs had almost the same reaction rate. An explanation for this finding is that some air leaked into the evacuated reactor or could have contacted the catalyst between runs. The effect of air on the catalysts will be further discussed later.

Effect of Special Treatment of the Reused Catalyst. The following treatments were given to various catalysts after they were used once to hydrogenate Oil C:

a) After Run 10-1, the oil and suspended catalyst in the reactor were evacuated to less than 0.5 mm Hg absolute pressure for ca. four hr. The oil was then removed from the reactor and filtered to recover the catalyst.

b) After Run 11-1, the oil and suspended catalyst were maintained under a hydrogen pressure of 5 psig for five hr before filtration.

c) Series 13 was made to study the effect of steam on the reused catalyst. Immediately after Run 13-1, the reactor containing the oil and catalyst was evacuated, and steam was introduced into the reactor to 5 psig pressure. Contact between the oil and steam was maintained for ca. 15 min, and the reactor was then evacuated to 0.5

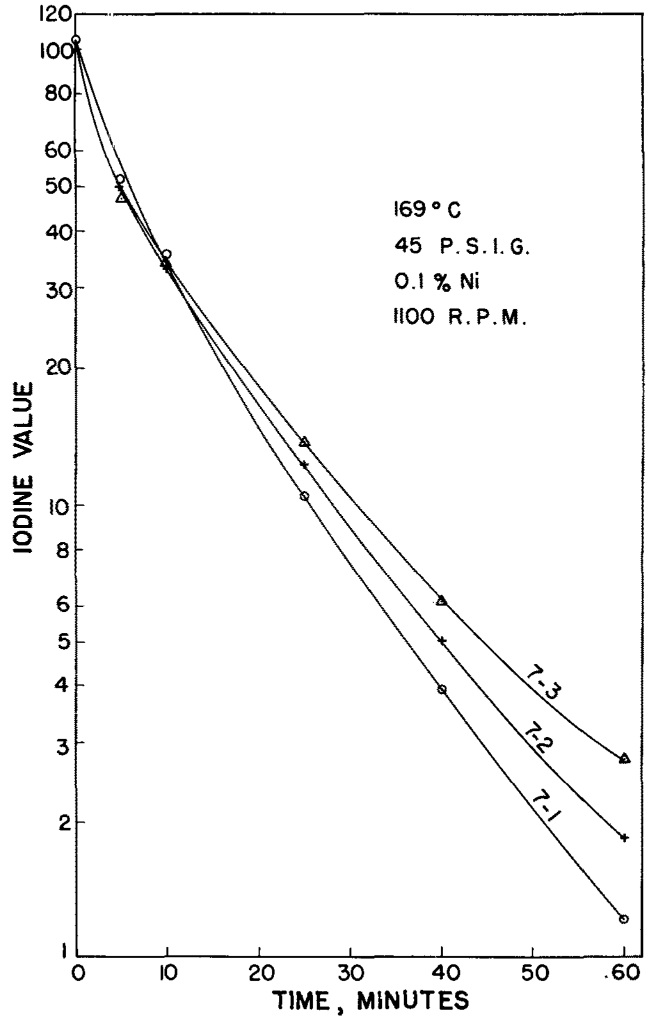

FIG. 3. Effect of reused catalyst on reaction rate at 169C.

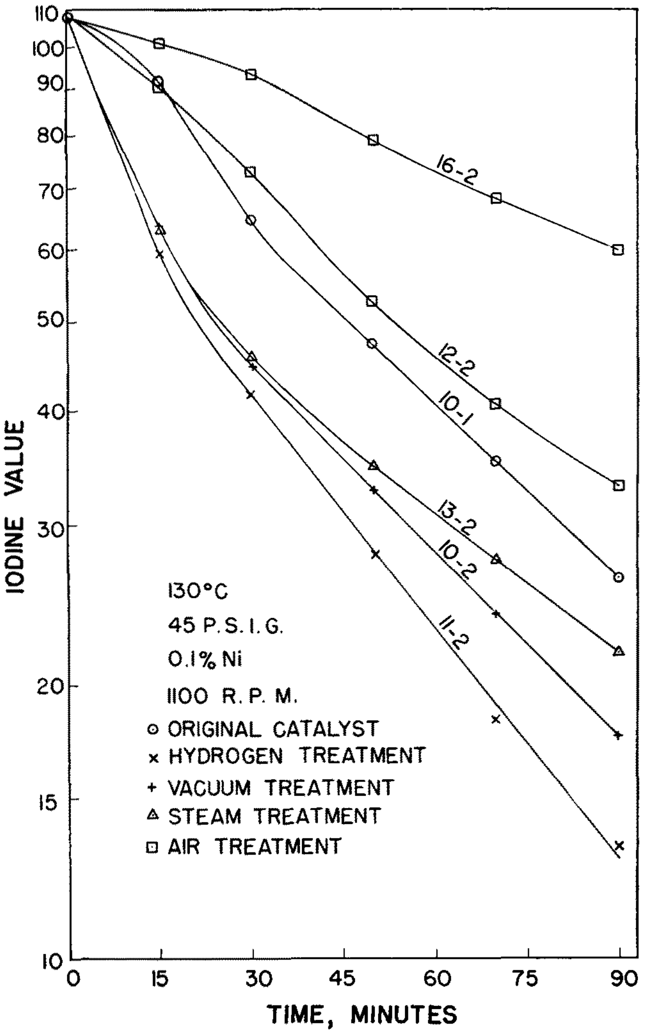

FIG. 4. Effect of special treatment to reused catalyst on reaction rate at 130C.

mm Hg to remove traces of the steam. Hydrogen was then introduced into the reactor in order to flush the oil from the reactor, and the mixture of oil and catalyst was filtered to recover the catalyst which was reused in Run 13–2.

d) In Series 12 and 16, the used catalysts were treated with air. In one test, the catalyst and hydrogenated oil from the previous run were contacted with air in the reactor. In the second test, the catalyst and the hydrogenated oil were removed from the reactor and then vigorously agitated while in contact with air. In each test, the catalyst was filtered from the hydrogenated oil, and the catalyst was reused.

Figure 4 indicates the results of the runs with reused catalysts at 130C. Run 10–1 indicates a typical run with fresh catalyst. The activity of the used catalyst was highest for Run 11–2 with the hydrogen-treated catalyst. Air-treatment (Runs 12–2 and 16–2) definitely decreased the catalyst activity. The activities of the steam-treated (Run 13–2) and the vacuum-treated (Run 10–2) catalysts were intermediate, but were higher than the activity of the catalyst for Run 10–1.

Selectivity and Isomerization with Used Catalyst. The composition of hydrogenated oils is shown in Figure 5 for Series 5 at 130C and in Figure 6 for Series 7 at 169C. Selectivity, as indicated by the total oleic or the linoleic acid content, decreased with catalyst use. At 130C, the selectivity ratio (The selectivity ratio is defined as the relative rates of hydrogenation of the di-unsaturated fatty acid groups in the triglycerides as compared to the mono-unsaturated groups.) (1) decreased from ca. 7.0 for first-use catalyst (Run 5–1), to 4.0 for third-use catalyst (Run 5–3), and finally to 3.0 for fifth-use catalyst (Run 5–5). At 169C, the ratio decreased from approx 9.5 for first-use catalyst (Run 7–1) to 7.5 for third-use catalyst (Run 7–3). *Trans*-isomerization decreased significantly with catalyst use at 169C, but no observable change was noted at 130C.

The results of Runs 10–2, 11–2, 12–2, 13–2 and 16–2 were compared. No difference was noted in the selectivity or isomerization for these runs with second-use catalyst regardless of the hydrogen, vacuum, steam, or air treatment of the catalysts.

Discussion of Results

Mass transfer resistances of the reactants to the catalyst surface were probably essentially eliminated in the present investigation. Hence differences of the kinetics, selectivity and isomerization between new and used catalysts can be attributed to changes on the catalyst surface.

The use of vacuum after Run 10–1 probably caused some, if not all, of the hydrogen absorbed on the catalyst surface to be desorbed. However, treatment of

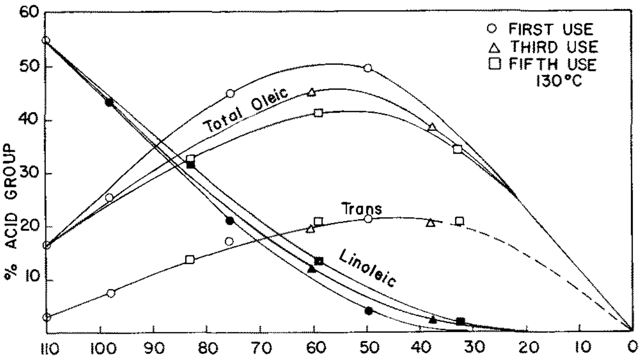

FIG. 5. Effect of reused catalyst on selectivity and isomerization at 130C.

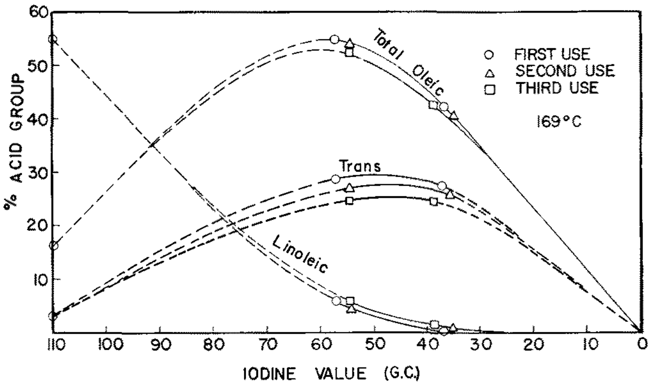

FIG. 6. Effect of reused catalyst on selectivity and isomerization at 169C.

the catalyst with hydrogen after Run 11–1 would presumably result in more absorbed hydrogen on the surface of the catalyst and is undoubtedly the reason for the increased catalyst activity. Steam treatment of the catalyst would also result in desorption of hydrogen. The results of Run 13–2 (after steam treatment) indicate a somewhat less active catalyst. Of course, steam may also have adsorbed on the surface, which could be harmful; any such adsorbed water is however apparently not a serious catalyst poison.

The extremely detrimental effect of air on the catalyst would probably be cause by two factors: 1) Oxygen or nitrogen could replace adsorbed hydrogen on the surface; and 2) The nickel and oxygen could react to form a nickel oxide coating which is non-catalytic or at least less active.

Possibly some deactivation of catalyst was caused in all runs by air. In each case, the catalyst was filtered and exposed to air, as may also be the case in some plant operations. When the catalyst was vacuum-treated, there is also the chance that some air leaked into the reactor. Series 12 and 16 were terminated after the second runs so that it is not certain whether air treatment damaged the catalyst permanently. But, since fresh catalyst, believed to have picked up atmospheric oxygen during storage, was activated after the first run, it is possible that the poisoning by air was not completely permanent.

Wisniak and Albright (9) have proposed that the induction period is caused by colored materials and/or odoriferous compounds in the original oil which act to poison temporarily the catalyst. The present results, however, indicate that this explanation is not generally correct since an induction period would then be expected for second- or third-use catalysts as well as first-use catalyst. The induction period for first-use catalyst is probably caused instead by rapid activation of the catalyst with initial use. In this respect, Mars and co-workers (8) report that Raney nickel catalysts often decrease in activity with storage. Apparently such loss of activity is related to oxygen contact of the catalyst (or catalyst flakes) or to slow desorption of hydrogen from the catalyst surface. One producer of nickel catalyst is very careful to store all catalyst in an inert atmosphere until the catalyst is actually used. Other manufacturers of catalysts should perhaps give more attention to the protection of the catalyst. In addition, exposure of the catalyst to air should be eliminated as much as possible during plant operations, including filtration.

The k′ results clearly indicate that the activity of fresh catalyst was less than that of slightly used catalyst. The following comparison is of interest in indicating the time required to obtain the most active catalyst as a function of temp:

130C—third run
154C—start and middle of second run
169C—start of second run

High temperatures obviously activated the fresh catalyst more rapidly.

The increase of catalyst activity with the initial use followed by the eventual decrease of activity may be related to the activity of each catalyst site plus the number of active sites. Fresh catalyst would presumably have a maximum number of "active" sites. The number would decrease with use because of poisons, wearing-out, etc. Each site in order to have high activity would need an optimum concentration of hydrogen, part of which might be in a highly adsorbed state. Quite possibly the catalyst used did not have such a hydrogen concn until it had been used (and contacted) with hydrogen for a period of time. The higher concn of adsorbed hydrogen at each active site might be responsible for the somewhat lower selectivity and isomerization found with used catalysts.

The reason for the reappearance of an induction period after three uses of the catalyst for hydrogenation runs at 130C is not known. Gradual accumulation of poisons on the catalyst surface (7) might be a factor in destroying some of the more active sites. Possibly these highly active sites react quickly with temporary catalyst poisons, but the less active sites act much slower with such poisons.

The effect of treating the nickel catalyst with air, steam, hydrogen or vacuum may be interest to the commercial hydrogenators of triglycerides. Additional investigations are recommended in which the catalysts will be treated with known quantities of various catalytic poisons.

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REFERENCES

1. Albright, L. F., JAOCS *42*, 250–253 (1965).
2. Albright, L. F., C. H. Wei, and J. M. Woods *Ibid. 37*, 315 (1960).
3. Albright, L. F., and J. Wisniak, *Ibid. 39*, 14 (1962).
4. Bailey, A. E., "Industrial Oil and Fat Products," 2nd Ed., Interscience Publishers, Inc., New York, 1951.
5. Eckey, E. W., "Vegetable Fats and Oils," Reinhold Publishing Corporation, New York, 1954.
6. Eldib, I. A., and L. F. Albright, Ind. Eng. Chem. *49*, 825 (1957).
7. Golendeev, V. P., K. G. Bogareva, E. T. Bobkova and O. N. Dobiynina, Zhur. Priklad Khim. *31*, 1722 (1858).
8. Mars, P., Th. v. d. Mond and J. J. F. Scholten, Ind. Eng. Chem. (Product Research and Development) *1*, No. 3, 161 (1962).
9. Wisniak, J., and L. F. Albright, Ind. Eng. Chem. *53*, 375 (1961).

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